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INFLUENCE OF AMMONIUM SALTS ON THE CORROSION OF COPPER IN
POWDER FORM

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As we know, copper in powder form is highly susceptible to the action of various corroding agents. For instance, the storage of powdered copper with ammonium salts and other chemicals will accelerate its corrosion.

We have previously expressed the ^{opinion} theory (1) that the corrosive activity of ammonium salts in atmospheric corrosion, in the absence of direct contact with the corroded surface, must depend upon the volatility of the acid forming ^{the} ~~that~~ salt. ^{in question.} This theory was formulated on the basis of a study of the corroding effect of only two salts: ammonium chloride and ammonium carbonate. It seemed useful, therefore, to check the correctness of the expressed point of view on a wider number of subjects. In the present work we tested the corroding action of chemically pure ammonium ^{halides} ~~halogens~~ and also of ammonium acetate, ammonium nitrate, ammonium carbonate, ammonium ^{disubstituted} sulfate and ammonium-diphosphate.

We tested common copper powder of factory make, containing 99.92 percent of copper and having a ^{gross bulk} dry weight of 0.9. [^{of} sp. wt.]

The corrosion tests were conducted as follows. Small porcelain ^{pan} cups containing portions of copper powder, and other ^{parts} cups

containing -- separately -- ammonium salts and water, were placed in glass jars of 2.5 litre capacity. The portions of copper powder were all of identical weight -- 2.5 grams each. The portions of salts were prepared from the measured quantity of 1 gram of ammonium (NH_4). The jars were then tightly closed with paraffin-soaked cork stoppers, sealed with paraffin, and placed in a thermostat. The corrosion experiments were conducted in a temperature of 40 ± 0.5 degrees for a period of twelve hours. The samples were then transferred to an exsiccator with calcium chloride as the drying agent, cooled and weighed until the weights became constant. The speed of corrosion was expressed in the ratio of milligrams to a gram of sample in 24 hours $\left(\frac{\text{mgs.}}{\text{g x 24 hrs.}} \right)$.

The effect of corrosive action of ammonium salts was determined as being the relation of the weight increase of a specific portion to the original weight, expressed in percent.

Results of the experiments are shown in Table I. The data shown are averages of four readings; the readings did not differ from each other by more than 10 to 15 percent.

Table I

Corrosive Action of Ammonium Salts on Copper in Powder Form
(12 Hour Exposure, Temperature 40 ± 0.5 Degrees Centigrade)

Salt	Copper portion (g)	Weight increase (mgs)	Corrosion speed $\left(\frac{\text{mgs}}{\text{g} \times 24 \text{ hrs.}}\right)$	Effect of corrosive action (%)	
ammonium {	chloride	2.5	53.2	42.56	2.12
	bromide	2.5	42.9	34.03	1.71
	iodide	2.5	43.4	34.72	1.73
	fluoride	2.5	21.4	17.12	0.84
	acetate	2.5	90.0	72.00	3.60
	nitrate	2.5	11.1	8.88	0.44
	carbonate	2.5	299.9	239.12	12.00
	sulfate	2.5	9.3	7.44	0.37
	diphosphate	2.5	14.6	11.68	0.58

Table I shows that the corrosive actions of different ammonium salts are not identical and depend upon the nature of the acid forming the salt.

So far as atmospheric corrosion is concerned here, its speed will be determined by the thickness of the liquid adsorption layer on the surface of the metal and the quantity of vapors and gases dissolved in it (2). In this case the formation conditions of the liquid adsorption film on any of the tested salts are absolutely identical; consequently, the thicknesses of the various layers are also equal. Thus, the observed differences in the corrosion speed depend solely upon the quantity and quality of vapors and gases dissolved in the

liquid adsorption layer. The latter is formed in the reaction atmosphere as the result of a partial decomposition of ammonium salts in connection with their thermal instability. Consequently, in general the corrosive action of an ammonium salt is the highest when its thermal stability is the lowest.

The character of the thermal decomposition of ammonium salts is determined by the properties of the acid forming the anion -- by its volatility. Salts formed by non-volatile acids (H_2SO_4 , H_3PO_4) liberate only ammonia upon decomposing, while ammonium salts of volatile acids (HCl , H_2CO_3) liberate acid vapors as well. Therefore the corrosive action of ammonium salts from volatile acids is usually much higher than that of salts formed from non-volatile compounds. This fact is well confirmed by the data in Table II, in which the effect of the corrosive action of various ammonium salts is related to the boiling points of the acids forming these salts.

Table II

Relation of the Corrosive Action of Ammonium Salts
to the Volatility of the Acids Forming Them

Studied Phenomena	Salts					
	NH_4Cl	NH_4Br	$(NH_4)_2CO_3$	NH_4NO_3	$(NH_4)_2SO_4$	$(NH_4)_2HPO_4$
Corrosive Action (%)	2.12	1.71	11.10	0.44	0.37	0.58
Boiling Point of	-85	-68.7	-65	84	338*	250*
Acid (Deg. C.)						(Decomposition)
(*Boiling Point of a 98.3% mixture)						

With ammonium salts of similar structural type, the thermal stability augments the power of the acid from which they are formed.

In the acid series HJ-HBr-HCl-HF, the thermal stability diminishes from HJ to HF (3). On this basis one could expect the aggressive influence of these salts to grow in the same order. In the case of ammonium fluoride, however, we observe a departure from the rule, apparently explainable through the lesser volatility of HF in comparison with the other haloid hydrides (the boiling point of HF is 19.5 degrees Centigrade, while that of HCl is 85 degrees Centigrade.)

Thus the volatility of the acid forming the anion of ammonium salt is the basic factor determining the extent of corrosive action of ammonium salts on powdered copper.

The presence of water vapors furthers the decomposition of ammonium salts. Apparently, the decomposing action of water intensifies as the extent of hydrolysis of a given salt widens. For instance, when ammonium carbonate is 80 percent hydrolyzed, the corrosive action is 11 or 10 percent. At the same time, when ammonium chloride is 0.14 percent hydrolyzed, the corrosive action is 2.12 percent.

It is evident that these factors -- volatility of the acid, thermal stability of the salts and their hydrolytic splitting -- do not exhaust the complexity and variety of the described phenomenon. Doubtlessly, the hygroscopic qualities of salts and the solubility of the acid vapors in the liquid adsorption film are also important factors which must be taken into consideration.

CONCLUSIONS

It is shown that the volatility of the acid forming an anion of salt is the fundamental factor determining the corrosive activity of the salt.